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Catalytic Conversion of Empty Fruit Bunch of Palm Oil for Producing Lactic Acid

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Abstract

Catalytic conversion of lignocellulosic biomass such as Empty Fruit Bunch (EFB) of Palm Oil into valuable chemicals such as lactic acid (LA) is an alternative route to currently fermentation route and it is a sustainable process for substituting petro-based chemical with biomass-based chemical. Conversion of lignocellulosic biomass (EFB) was conducted in a 100-ml batch reactor in aqueous solution using homogeneous $AlCl_3$ catalyst at mild temperature in the range of 140-240^oC, under hydrothermal condition. Some chemicals are identified in the product especialy LA and levulinic acid which are valuable chemicals produced by hydrolysis of lignocellulosic biomass and yield of LA compared with cellulosic biomass for comparison of feedstock. The sugar units in the lignocellulosic biomass (EFB) was around 48.75%, dominated by glucose (28%), xylose (16.5%), and followed with lower composistion of other sugar units such as galactose (1%), arabinose (2.5%) and mannose (0.75%). The yield of EFB conversion to lactic acid was found in the range 6-8.9% at temperature 140-240^oC while for cellulosic material 19%, with reaction time 3 hours and range of fixed $AlCl_3$ concentration 50-100 mM. Experimental results show that higher operating temperature and higher concentration of catalyst will produce higher percentage of LA. However, pretreatment of lignocelluloses with NaOH produced lower yield of LA 3.18 to 5.69 % and probably the pretreatment leading to degradation of sugar units in the biomass.

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Keywords: catalytic conversion of lignocellulosic biomass; Lactic Acid; hydrolysis; homogeneous catalyst

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1. Introduction

Recently, production of lactic acid from bio-based resources has increased owing to growing polymer markets, increasing demand in the chemical sector as well as many applications in the food industry requiring lactic acid as the feedstock [1, 2, 3]. On the other side, research in a catalytic conversion of cellulosic biomass has increased significantly during the last decade [5, 7, 8, 9]. This is due to catalytic chemical conversion is quite fast compared to currently fermentation route and it is also a sustainable process for substituting petro-based chemical with biomass-based chemical. However, the selectivity of catalytic conversion becomes limiting step in applying of the process to industrial scale [9]. The higher yield of conversion or decomposition of biomass to valuable components, such as lactic acid and levulinic acid has put more weight on catalytic conversion rather than fermentation route. The alternative process to fermentation route of producing lactic acid by applying chemical conversion from biomass is needed because it is also a sustainable process and it makes use of abundant and less valuable biomass or waste biomass. Hence, the chemical conversion will be an opportunity for supplying accelerated need of lactic acid in the future.

A number of literature [3, 7, 11] reported significant yield of lactic acid production from biomass by employing homogenenous catalyst such as transitional metal such as (Zn(II), Ni(II),Co(II) and Cr(III)), and recently using La (III), Pb (III) for biomass conversion or decomposition in hydrothermal condition at sub-critical water (300^{o}C) as well as at superciritical water. Further, Rasrendra (2012) recently reported that low hydrothermal condition for chemical conversion of biomass, mainly triose, has been possible to be converted to lactic acid by using homogeneous catalyst $AlCl_3$. This mild condition will be an advantage in carrying out conversion of biomass to lactic acid.

The objective of this paper is to apply metal salts, especially $AlCl_3$ conversion of abundantly available lignocellulosic biomass such as empty fruit bunch of palm oil (EFB) to lactic acid in aqueous solutions, at mild to high operating condition, temperature 140-240^{o}C, under hydrothermal pressure of water using $AlCl_3$ as the catalyst and then determine yield of conversion with respect to lactic acid. Further, the role of pretreatment of lignocellulosic biomass in catalytic conversion of EFB is also studied. The yield of LA from cellulosic biomass was produced for comparison of feedstock.

2. Experimental Method

Experimental method was conducted first for determination of carbohydrate in the form of sugar units for lignocellulosic biomass (EFB) as the feedstock before converting it to lactic acid. The experiment is a very crucial step for calculating the monosaccaride polymer in the biomass, especially convertible sugar. Procedure follows the method of two stage of hydrolysis by US National Renewable Energy Laboratory (NREL). The first stage hydrolysis was conducted by soaking lignocellulosic biomass, in the form of fibre, into concentrated sulphuric acid 72 % (w) at temperature 30^{o}C for 60 minutes and was followed with second stage hydrolysis of hydrolisate in aqueous sulphuric acid 4% (w), at temperature 105^{o}C for about 60 minutes.

An HPLC with a selected column (Biorad Aminex 87H dan 87P) was used for determining sugar units such as glucose, galactosae, xylose, arabinose, manose. The HPLC was equipped with a Refractive Index (RI) detector. Aqoueous sulphuric acid (5 mM) and water was used as mobile phase for Biorad Aminex 87H dan 87P, respectively. The flowrate of mobil-phase was set on 0.6 ml/min for both columns. The HPLC with column Biorad Aminex 87H was operated at temperature 60 °C for analysis of glucose while for analysing other sugar units with column Biorad Aminex 87P operated at temperature 80 °C.

The experiment was then followed by production of lactic acid from EFB. A wide range of homogeneous catalysts in the form of metal salts has been tested earlier for the conversion of triose to LA in water (Rasrendra et al., 2011) and $AlCl_3$ catalyst was found to produce the highest conversion into LA production. Therefore, $AlCl_3$ was selected as the catalyst for the conversion of EFB to produce LA. The reactions were performed in a 100-ml batch reactor at varying temperature of 180^{o}C to 220^{o}C using 2,5 wt% biomass loading in aqueous solution containing 0.1 M $AlCl_3$ as the catalyst. The equipment consists of a 100-ml batch reactor for conducting hydrolysis and equipped with a heater and a thermocontroller connected to the heater for controlling the reactor temperature. The operating

pressure of reaction was resulted from hydrothermal condition due to pressure of steam produced in the reactor. The EFB is obtained from plantation in Sumatera Island, Indonesia. The EFB was cut into 5 cm length and then the fibre was separated from dirt. The fibrous size was further reduced with ball mill into 100 mesh size. The fibre was fed into reactor containing aqueous solution with catalyst $AlCl_3$. The temperature of reactor was varied around 180 to 220^{o}C. The reaction time is set at 180 min for all reactions.

The conversion of lignocellulosic biomass (EFB) into LA was investigated by analyzing reaction mixture using HPLC with respective column with external LA standard for calibration. Note that only LA from the product of chemical conversion was measured in the HPLC because it is the main interest of conversion studied in this paper. The yield of LA from lignocellulosic biomass (EFB) conversion was calculated from dividing LA produced by loading mass of feedstock. Cellulosic of filter paper was also used as feedstock for hydrolysis conversion. Other experiments were conducted by soaking the lignocellulosic biomass into aqueous solution containing NaOH with varying molarity for about 15 minutes. The biomass was fed into the reactor containing aqueous solution with catalyst $AlCl_3$.

3. Results and Discussion

3.1. Determination of carbohydrate composition in lignocellulosic biomass

Figure 1 shows the result of carbohydrate composition from the EFB, shown in the form of monosaccharide polymer. Sugar units in the fibre is mostly dominated by glucose (28%), xylose (16.5%), and followed with lower composistion of other sugar units such as galactose (1%), arabinose (2.5%) and mannose (0.75%). The other composition of EFB is lignin and extract was not determined in this experiments. Total sugar composition of convertible sugar sums up to about 48.75% and quite comparable with other results for lignocellulosic biomass [11]. Specifically, most of biomass such as fibre from coconut mesocarp or corn cob, comprises 32-43 % (w) of cellulose and 10-20 % (w) of hemicellulose and from the calculation above, the cellulose in the EFB was around 28% and the results is quite comparable to previous results for lignocellulosic material. Hence, the experimental results shows that the EFB can be classified into hemicellulosic and cellulosic component, as they are all hydrolysed into sugar units up to 48.75%, determined by the method above.

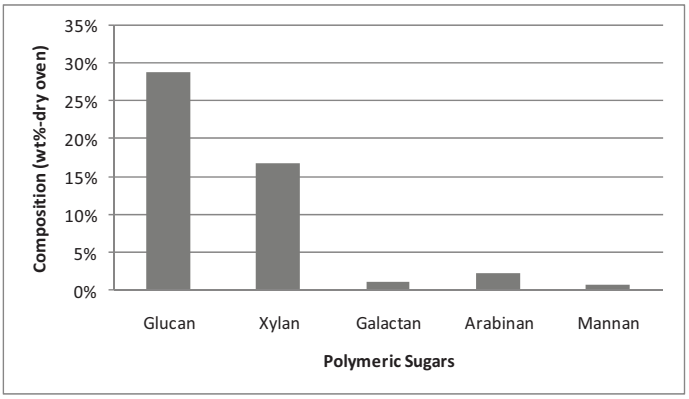

Fig. 1. Result of sugar units in monosaccharide polymer from lignocellulosic biomass (EFB)

3.2. Conversion of lignocellulosic and cellulosic biomass to LA using homogeneous catalyst

In the preliminary experiment, the product of hydrolysis after 3 hours of reaction time was unloaded from the reactor. The product mixture was reddish solution (visual appearance) with insoluble materials remaining in the end of reaction. The solution mixtures were then separated from the insoluble materials by filtration for further

quantification of the main reaction products. The conversions of the EFB are presented in Table 1, as converted into LA yield for temperature range of reaction, 413 K to 513 K ((140 - 240^{o}C).

The yield of LA from non-treated lignocelluloses is in the range of 8.1 to 8.9% (Table 1, entry 1-2). The results are quite low compared with that from cellulose feedstock at a comparable operating condition (Table 1, entry 5, 19.38%). This difference may be caused by the amount of convertible sugars in the EFB. The convertible sugars in the EFB is only about 48.75 % (w) which half of the convertible sugar in the filter paper. Therefore, the yield of LA from EFB is about half from the yield of cellulose as the feedstock.

Tabel 1. Yield of LA from chemical conversion of EFB and cellulose

No	Feedstock	Loading of Biomass	Catalyst Concentration	Reaction Temperature (K)	Pressure (atm)	Yield of LA (%) w/w
1.	EFB	2.5%	0.1M	413	3.56	6.97
2.	EFB	2.5%	0.1M	453	10.03	7.50
3.	EFB	2.5%	0.1M	503	27.97	8.33
4.	Cellulose	0.5%	0.05M	463	13.39	8.16
5.	Cellulose	2.5%	0.1M	453	10.03	19.38
6.	Cellulose	5%	0.05M	453	10.03	12.64

The yield of LA from the EFB and cellulose obtained in this works is rather lower compared with the conversion of cellulose to LA using other metal salts [3, 11]. Wang *et. al.* reported high yield of LA (up to 80%) when using lead salts as the catalyst. Though Al-salts are reported as active catalysts for the conversion of triose to LA [7], it may provide competitive reactions on the conversion higher sugars precursors such as cellulose. The sugar units in the biomass may follow parallel reactions pathways to form other by-products such as intermediate 5-hydroxymethyl furfural (HMF) or glycolic acid, instead of through preferred trioses intermediates such as glyceraldehyde or dihydroxyacetone to form pyruvaldehyde and then converts to lactic acid [7]. The reaction scheme for the EFB and cellulose conversion is shown in Figure 3. This scheme suggests that the role of catalyst plays important role on determining reaction selectivity. Hence, the role of catalyst can be defined as promoting effect for cellulose or hemicelluloses depolymerisation as well as its role for Lewis acid is required for converting the biomass into preferred platform chemical lactic acid. Meanwhile, the side reactions due to Bronsted acidity should be minimized. Further attempts to improve reaction selectivity by in-depth catalysts study are in progress and will be reported in due course.

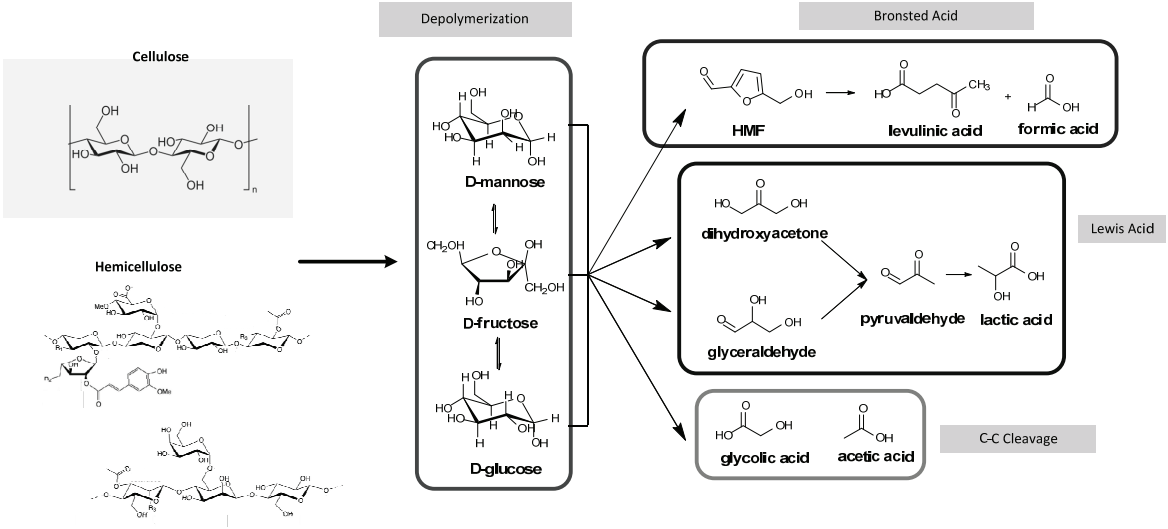

Figure 2. Simplified scheme to explain the preferred reaction network in the conversion of convertible sugar into lactic acid (modified from

Rasrendra, 2012)

Apart of catalyst activities, the presence of lignin in the feedstock could influence on the conversion of EFB to lactic acid. In order to verify influence the lignin on the conversion of EFB to LA, further experiments were conducted using pretreated EFB. The EFB were soaked with NaOH in the range of 0.1 M to 0.5 M at temperature for 140^{o}C for 15 minutes prior to reactions. After the pretreatment, the EFB was washed and dried before used as the feedstock for subsequent conversion to LA using $AlCl_3$ as the catalysts. Table 2 presents the experiments results using pretreated EFB. Though it is expected that NaOH provides delignification effect of the EFB, the yield of LA is found only to be around 3.18 to 5.69 %. These yields are relatively low even compared to non-treated EFB. These results indicate that NaOH-pretreatment does not provide positive influence on the conversion of EFB to LA. The Lewis acid role of $AlCl_3$ seems not exhibited during the conversion of pretreated EFB using NaOH. Furthermore, the NaOH pretreatment does not influence on the promoting depolymerization cellulose or hemicelluloses of EFB towards triose intermediates production. Hence, the choice of suitable catalyst with dominant Lewis acid property needs to be selected in the future with additional positive impact on the depolymerisation of polymeric sugars presence in the biomoss into their sugar units.

Table 2. Yield of LA from chemical conversion with feedstock of EFB treated with NaOH

No	NaOH (M)	$AlCl_3$ (M)	Loading of Biomass	Rection time	Temp (K)	yield of LA, % (w/w)
1	0.1	0.1	5%	3 hours	453	5.69
2	0.1	0.1	5%	3 hours	503	3.17
3	0.5	0.1	5%	3 hours	453	6.21
4	0.5	0.1	5%	3 hours	503	3.18

4. Conclusion

Characterization of carbohydrate composition from lignocellulosic biomass (EFB), was shown in the form of monosaccharide polymer comprising sugar units in the fibre such as glucose (28%), xylose (16.5%), galactose (1%), arabinose (2.5%) and mannose (0.75%) with total sugar composition of convertible sugar sums up to about 48.75%.

The yield of EFB conversion to lactic acid was found in the range 6-8.9% at temperature 140-240^{o}C while for cellulosic material 19%, with reaction time 3 hours and range of fixed $AlCl_3$ concentration 50-100 mM. Experimental results show that higher operating temperature and higher concentration of catalyst will produce higher percentage of LA. However, pretreatment of lignocelluloses with NaOH produced lower yield of LA 3.18 to 5.69 % and probably the pretreatment leading to degradation of sugar units in the biomass.

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